SCIENCE FOR CERAMIC PRODUCTION

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SYNTHESIS OF NEODYMIUM-CONTAINING PIGMENTS

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Synthesis of ceramic pigments with equimolecular ratios of oxides ($Nd_2O_3 : P_2O_5$, $Nd_2O_3 : ZrO_2$, $Nd_2O_3 : TiO_2$) was investigated. It was shown that these oxide ratios allow obtaining pigments of different palettes suitable for coloring glazes.

Investigators have recently turned their attention to the use of rare-earth elements for decorating porcelain and synthesis of ceramic pigments [1].

The use of high-temperature coloring oxides, Nd_2O_3 in particular, allows expanding the palette of heat-resistant pigments. Neodymium oxide is characterized by the following indexes: density of 6.59 g/cm^3, melting point of 2320°C, light-blue color.

Pigments of different crystal structure and with different physicochemical properties can be made from neodymium(III), zirconium, titanium, and phosphorus oxides.

When neodymium and zirconium oxides react at temperatures above 1550°C, neodymium zirconates, $Nd_2Zr_2O_7$, are formed with a structure of the fluorite type. Neodymium titanates, Nd_2TiO_5, are formed with an equimolecular ratio of the oxides through the intermediate stage of $Nd_2Ti_2O_7$. The compound obtained, Nd_2TiO_5, can crystallize in three different structures as a function of the ion radius and temperature: rhombic, hexagonal, and cubic.

Neodymium orthophosphates are obtained in heating with neodymium(III) oxide and ammonium hydrophosphate with a monoclinic structure at 1100 – 1200°C. Polymorphous transitions, which cause more intensive solid-phase reactions with the indicated oxides, are characteristic of neodymium oxide, especially if it is in the cubic system. In this case, the crystal lattice contains up to 25% vacant anion vacancies. On heating, ions diffuse through these vacancies, which is energetically more advantageous for solid-phase reactions with formation of a compound with new crystallization centers around which crystals grow.

Nd_2O_3, ZrO_2, and TiO_2 were used as the initial components, while P_2O_5 was incorporated through monosubstituted ammonium phosphate. All reagents were analytically pure. Compositions with equimolecular amounts of oxides were selected for the study (see Table 1).

The results of the study of the systems by differential thermal analysis are shown in Fig. 1. The maximum temperature of synthesis of the pigments was 1000°C.

Endothermic effects which are absent in other mixtures are observed in mixtures of neodymium and phosphorus oxides (Composition 1). The deep endothermic effect at 185 – 240°C corresponds to decomposition of monosubstituted ammonium phosphate.

The other endothermic effects on the DTA curve are characteristic of polymorphous transitions of neodymium oxide. An exothermic effect caused by formation of $NdPO_4$ is observed at 900°C and was confirmed by x-ray phase analysis.

Exothermic effects at 650 – 730°C are observed in the mixture of neodymium and titanium oxides (Composition 3), probably due to formation of neodymium borates. At higher synthesis temperatures, $Nd_2Ti_2O_7$ of perovskite structure is formed [3]. Our petrographic studies showed that the compound crystallizes in rhombic form with a refractive index

TABLE 1

Composition*	Content, moles				Color of pigment after firing (visually)
	Nd_2O_3	P_2O_5	ZrO_2	TiO_2	
1	1.0	1.0	–	–	Pink
2	1.0	–	1.0	–	Pinkish-lilac
3	1.0	–	–	1.0	Lilac

* All compositions contained added 3.0 wt.% B_2O_3.

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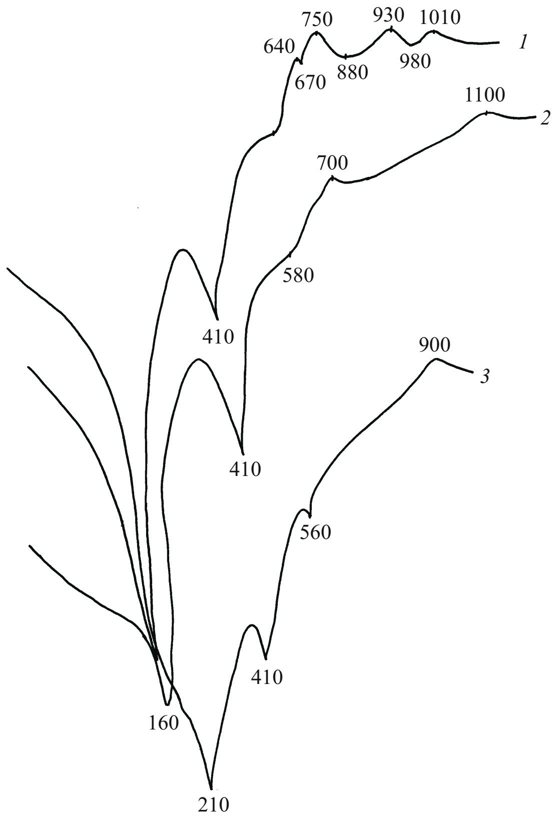

Fig. 1. Derivatograms (°C) of neodymium-containing pigments with TiO_2 (*1*), ZnO (*2*), and P_2O_5 (*3*) additives.

close to the refractive index of rutile ($n_d = 2.65$). However, the amount of neodymium pyrotitanate is a maximum of 20%.[2]

In addition to neodymium pyrotitanate, rutile (crystals of fibrous habit) and neodymium(III) oxide in the trigonal form are present. $Nd_2Ti_2O_7$ is most completely separated only at a higher synthesis temperature. Insignificant diffraction maxima belonging to $Nd_2Ti_2O_7$, Nd_2O_3, and rutile are observed in the x-ray diffraction pattern (Fig. 2).

A solid solution is formed in synthesis of pigments in the $Nd_2O_3 – ZrO_2$ system. In the unit cell, some of the neodymium atoms are substituted by zirconium atoms which additionally introduce oxygen atoms. This solid solution is unstable and is a function of the composition and temperature. At temperatures above 1500°C, it changes into the final product, $Nd_2Zr_2O_7$.

The line x-ray pattern (see Fig. 2) has diffraction maxima belonging to both the oxides (Nd_2O_3 and ZrO_2) and the compound $Nd_2Zr_2O_7$. However, the reaction of formation of the compound $Nd_2Zr_2O_7$ is incomplete. Maxima corresponding to titanium and zirconium oxides and zirconium titanate are also observed.

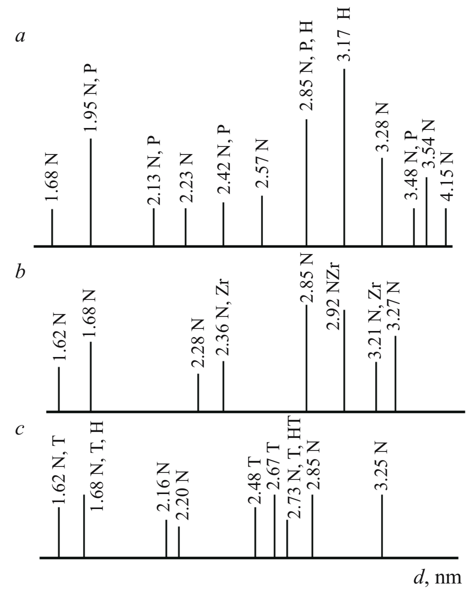

Fig. 2. X-ray patterns of neodymium-containing pigments with P_2O_5 (*a*), ZrO_2 (*b*), and TiO_2 (*c*) additives: N) Nd_2O_3; T) TiO_2; Zr) ZrO_2; H) Nd_3PO_4; HT) $Nd_2Ti_2O_7$; NZr) $Nd_2Zr_2O_7$.

Mineralizers, boron oxide in the amount of 3% in particular, affects the occurrence of the solid-phase reactions. Complete formation of neodymium phosphate takes place in the presence of boron anhydride (3%) in a 1 : 1 molar ratio of the oxides at a synthesis temperature of 1200°C. The simultaneous presence of neodymium, zirconium, and titanium oxide in the form of rutile is observed in synthesis of pigments using other oxides.

Industrial tests of the pigments were conducted with glazes for ceramic wall tiles. It was found that the brightest color is obtained when 7 – 10% pigments of the dry weight of the glaze is added.

REFERENCES

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3. A. I. Mikhailichenko, E. B. Mallis, and Yu. S. Patrikeev, *Rare-Earth Metals* [in Russian], Metallurgiya, Moscow (1987).

[2] Here and below: mass content.